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COLD CLIMATE OIL SPILLS: A TERRESTRIAL AND FRESHWATER RESEARCH REVIEW

by

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The first part of this study reviews world-wide research on cold climate oil spills on land to identify some of the terrestrial environmental factors in cold regions affected by oil spills and some of the techniques for measuring impacts and terrestrial systems, primarily soils. The second part of the study reviews cold climate research on oil spills into fresh water, and notes that remarkably little baseline information is available. The final part of the report, which surveys Alaskan hydrocarbon spills in the period January 1974 through May 1976, concludes that almost all of the spills investigated were of refined products (since they were most likely to be spilled in inhabited areas). These studies will be of interest to all those concerned with cold climate oil spills on land and into fresh water.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

The first part of this study reviews world-wide research on cold climate oil spills on land to identify some of the terrestrial environmental factors in cold regions affected by oil spills and some of the techniques for measuring impacts and terrestrial systems, primarily soils. The second part of the study reviews cold climate research on oil spills into fresh water, and notes that remarkably little baseline information is available. The final part of the report, which surveys Alaskan hydrocarbon spills in the period January 1974 through May 1976, concludes that almost all of the spills investigated were of refined products (since they were most likely to be spilled in inhabited areas). These studies will be of interest to all those concerned with cold climate oil spills on land and into fresh water.

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PREFACE

In July 1975 the U. S. Environmental Protection Agency gave a Grant to the University of Alaska to investigate existing technology, research efforts, effectiveness of conventional oil spill cleanup equipment, availability of experienced people, and probable oil spill impact areas in the state of Alaska. The focus of the one year study was to be on shoreline habitats endangered by both onshore and offshore petroleum extraction, transportation and exploration activities. The study was to elucidate priority areas needing research and development attention.

Owing to a series of setbacks, some related to the nature of operating in Alaska and others relating to the perversity of fortune, the goals of this study gradually narrowed down with the passage of years. What finally emerged were three studies which are presented together as Parts 1, 2, and 3 of the present volume.

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ABSTRACT

Part 1 is a review undertaken to identify some of the terrestrial environmental factors affected by oil spills and the techniques for measuring impacts and terrestrial systems, primarily soils. This cold region technology has applications for both determining the degree of damage and also monitoring recovery of sites affected by spilled oil. This review includes findings as well as notations of research needs. Areas covered in the review are Albedo, Energy Budgets, Active Layer Responses to Oil Spills in Cold Regions, Oil Movement in Soil, Oil Measurement in Soil, Microbial Degradation of Oil in Cold Soils, Fertilizer Additions, Microbial Innoculation, Aeration, Degradation of Oil Fractions, Temperature Effects, and Units of Measure.

Part 2 is a review of North American Arctic and Subarctic oil spill research in fresh water. The areas considered are algae, macrophytes, zooplankton, benthic invertebrates, fishes and decomposers. The section on general research needs points out that the most critical need for further research on the effects of oil spills into fresh water ecosystems in the north is for baseline-type studies. This section points out that in Alaska there are over three million lakes larger than 8 hectares. As late as 1977 only about 150 have been given even the most cursory examination. There is some evidence that the trophic system of lake classification may not be applicable in Arctic and Subarctic Regions. Also in 1977 less than a score of the more than 900 streams listed in Alaska can be considered to be known. Of those, probably less than five are well known. Only 27 stations are included in the U.S.G.S. National Water Data Network in Alaska compared to 498 in the contiguous 48 states despite the fact that about one-third of U.S. river flow occurs in Alaska.

Part 3 is a survey of hydrocarbon spills reported in Alaska in the period 1974 through May 1976. More than 99 percent of the hydrocarbons reported spilled in the period investigated were of refined products. This, in part, may be explained because crude spills are often likely to occur in uninhabited regions. Much of the research today has been carried out with crude oil. Since many refined products cause more environmental damage than crude oils, perhaps the research priority should be reconsidered in the light of these figures.

This report was submitted in fulfillment of Grant No. R803843 by the University of Alaska under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 1975 through December 1979. The work was completed in April 1980.

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COLD-REGION OIL SPILLS: A REVIEW OF IMPACT ASSESSMENT OBJECTIVES AND TECHNIQUES

By

Jay D. McKendrick

and

Thomas E. Loynachan

INTRODUCTION

The concern for oil spill damages and resulting pollution of environments has a relatively recent history in the U.S. and worldwide. The technology and research of oil spills in cold regions of the U.S., primarily Alaska, has an even shorter duration. This review was undertaken to identify some of the terrestrial environmental factors affected by oil spills and the techniques for measuring impacts on terrestrial systems, primarily soils.

The technology has application for both determining the degree of damage and also monitoring recovery of sites affected by oil. This review includes findings as well as notations of research needs.

Albedo, Energy Budgets, and Active Layer Responses to Oil Spills in Cold Regions

Several scientific groups in Alaska and Canada have reported and are engaged in studying various influences of oil spills on energy regimes of terrestrial sites. There were two main considerations: (A) that oil spills would increase solar energy absorption resulting in degradation (thermokarst) in ice-rich permafrost areas, and (B) oil spills would cause increased heat absorption and in turn increase latent and sensible heat fluxes which may derange regional climates. The geographical locations of such studies must also be considered. Experiments have ranged between taiga and arctic tundra; both zones contain permafrost conditions, but active layer thickness, vegetation, and

degrees of natural disturbances vary substantially between those types.

Thermokarst problems may be less of a general threat than previously believed for cold regions. Ives (1970) suggested that tundra fragility was approximately proportional to the permafrost ice content and inversely proportional to the mean annual ground temperature. Therefore, the least fragile areas would be dry mineral outcrops, and the most fragile areas would be medium- to fine-grained sediments and organic soils where annual average temperatures approached 0° C.

Increases in active layer thickness at Richards Island, Norman Wells, Tuktoyaktuk, and Inuvik due to oil spills were estimated at approximately 22%, according to Mackay, Charles, and Phillips (1975). They also noted that due to variation, probing could only detect active layer increases greater than 10%. Also, that technique had limitations in rocky and gravelly soils. Their discussions of oil spills affecting heat flux, thermal conductivities, and surface temperatures of taiga and tundra is currently the most thorough.

Haag and Bliss (1974) presented informative energy budget data for tundra sites affected by oil spills and certain other disturbances. They concluded that for tundra areas, depth of peat appeared to be the principal factor controlling ground temperature and thaw penetration. Furthermore, vegetation cover had little effect on the radiant energy balance since the living vegetation mass was small. In permafrost regions, the killing of surface vegetation by contact with oil may not, by itself, lead to increased thawing; and surface cultivation that would disrupt the peat layer may cause more serious environmental damage due to thermokarsting than leaving the oil in soil in an unaltered state.

Unpublished observations by the staff of the Agricultural Experiment Station, University of Alaska, indicate that at a scraped, tilled site near Prudhoe Bay, the surface horizon has continued to slump several years following the initial perturbation. This was presumably due to a substantial increase in depth of the active layer.

Preliminary studies reported by Wein and Bliss (1973) in Canada suggested that even though albedo declined due to oil treatments, the active layer remained constant; hence, thermokarst was of no consequence during the first year or two following a spill on arctic tundra in the Mackenzie Delta region. Haag and Bliss (1974) continued and expanded those studies and found albedo declined from 15% in controls to 7% on oiled plots and that latent heat dissipation depended upon available moisture at the soil surface. If the surface dried, latent heat loss declined and soil heat flux increased resulting in a net increase in active layer thickness. Where oil was applied, latent heat losses declined (presumably because of the hydrophobic nature of oil-soaked materials at the surface) and soil heat flux increased, causing an approximate 17% increase in active layer thickness. Apparently, a 17% increase in active layer thickness must not have caused severe thermokarst, otherwise Haag and Bliss (1974) would have noted such conditions in their report.

Effects of oil on active layer thickness has been examined at three arctic tundra sites on the Alaskan North Slope. The CRREL group (Deneke, et al., 1974) measured thickness of the active layer at the Cape Simpson seeps east of Barrow. They also monitored soil temperatures at those seeps and in the Barrow plots. Results of these studies indicated that

soil temperatures at the Cape Simpson seeps were 3-5° C warmer in the day and 1-2° C warmer at night on the oiled areas compared to the unaffected adjacent sites. Active layers in the oil-affected sites were about double those outside the seep. Soil temperatures on the Barrow oil spill plots are possibly available in a 1971 CRREL Technical Note by D. M. Vietor but apparently have not been published.

The Alaska Agricultural Experiment Station studies at Prudhoe Bay included measurements of active layer thicknesses in oil-treated plots. A small test of the effects of burning oil from ice-rich permafrost in 1973 failed to induce thermokarst even though all vegetation was killed. Apparently, the insulating properties of the peaty surface layer were retained even with the burning and oiling. Heat flux and albedo were not measured at the Prudhoe Bay plots.

The CRREL/EPA studies of oil spilled on taiga (Collins, et al., 1976) include monitoring soil temperatures. Increases in surface temperatures were commonly noted in taiga sites (Mackay, et al., 1975) and generally assumed to occur in all permafrost regions (Raisbeck and Mohtadi, 1974). Hutchinson and Hellebust at the Joint Canadian-Alaskan Arctic Workshop on the Prevention and Mitigation of Oil Spills (6-7 November 1974, Anchorage, Alaska) and Hutchinson, Hellebust, and Telford (1974) indicated that active layer thickness often changed more due to trampling by investigators than due to oil spills. Mackay, Charles, and Phillips (1975) noted that some of the largest increases in active layer thicknesses occurred on "botanical" spill plots where oil was sprayed uniformly over the vegetation compared to point spills.

Addison (1975) studied thermal effects of oil spills in the high

Arctic and noted heat flux and thaw increased 100% in moist meadows and as much as 200% in drier sites. He believed thermokarst could develop wherever the moss layer was destroyed. But apparently there are relatively few areas in the high Arctic where heavy moss layers form compared to the low Arctic.

Removing trees from a temperate-zone peat bog did not affect temperatures in the upper meter (Brown, 1976). Ecologists, modeling effects of off-road vehicles in arctic tundra predicted that compaction and vegetation removal would among other effects increase active layer thickness (Barkley, Miller, and Stoner, 1977).

Raisbeck and Mohtadi (1974) suggested that oil contamination lowers thermal conductivity of soil. Mackay, Charles, and Phillips (1974) indicated that oil could increase soil thermal conductivity as much as 10-20% by filling voids and compaction of the moss layer.

Everett (1978) recently reported that effects of oil increased thaw depth of wet tundra soils during the first year of a spill near Barrow, Alaska. Those effects apparently were not great enough to produce thermokarst. Furthermore, Everett (1978) concluded that the physical damages were relatively short-lived.

Therefore, the effects of oil on cold-region soils has not proven to be as serious a threat universally to thermokarst in the Arctic, neither have the various intricacies and implications been well-understood. Hence, there are yet unresolved points for study.

In 1970, G. A. McKay questioned the effects oil spills in the Arctic would have on tundra and taiga climates. His questioning was apparently based on assumptions that darkening the surfaces of arctic

landscapes would increase absorption of solar radiation, thereby upsetting normal sensible and latent heat fluxes, which could in turn change regional climatic patterns, if great enough in magnitude. Apparently, those concerns have persisted because the Committee to Evaluate NSF Arctic Programs (1977) ranked Arctic Basin and polar meteorology and climate second in an array of priority items that should be researched. Even though that committee failed to mention oil spills directly, heat balance, albedo, boundary layer mixing, and heat flux were itemized. Most of such concerns were possibly over potential massive spills on frozen oceans rather than terrestrial spills, which would be less extensive than spills on water, due to topography and surface properties.

Postulated changes in sea level and climatic patterns resulting from melting of the polar ice caps are plausible events from which people can readily identify consequences. For that reason there may be concerns for arctic marine oil spills in addition to potential threats to marine life.

Oil Measurement, Movement, and Degradation in Soil

In the event of a terrestrial oil spill, regardless of the degree of damage to biological organisms, the site can become repopulated through natural migration or non-assisted "seeding" whenever constraining conditions are alleviated. Because spilled oil contaminates soil, there can be no reinvasion of either plants or living oil-sensitive soil microbes until the soil is freed of damaging pollutants. Therefore, for both environmental damage assessment and monitoring habitat recovery,

oil content measurements of soil are unquestionably of supreme importance. The importance of terrestrial oil spills must not be minimized, (Vanloocke, et al., 1975). The soil scientist should be a central figure in any concerted terrestrial oil spill research group, regardless of prevailing climate.

The following contains findings on terrestrial oil measurement, movement, and degradation, primarily from North American arctic research effects.

The American Petroleum Institute published a review, "The Migration of Petroleum Products in Soil and Ground Water Principles and Countermeasures" (Davis, et al., 1972) to which we also direct the readers' attention.

Oil Measurement in Soil

Land forms and related topographical position in the Arctic and subarctic regions of North America are quite varied. These range from the low center and high center polygons in the relatively flat terrain of locations in the arctic coastal plain to the very steep and dissected inclines of mountainous regions. Following an oil spill on land, oil will flow away from the spill site until it is either contained in a natural basin or absorbed by the soil or ground cover. The quantity of oil spilled, the terrain, the time of year, the soil-moisture and organic matter contents, and the containment procedures (if any) will affect the quantity of soil-retained oil at any specific site within the spill. Collins, et al. (1978) reported that a summer spill on a subarctic forest site near Fairbanks, Alaska affected a larger area than a similar controlled spill applied during winter. Visually inspecting a spill may

be inadequate to predict the success of reclamation efforts particularly where subsurface oil movement occurs. Collins, et al. (1978) also noted that oil spilled in the summer moved greater distances laterally beneath the organic moss layer without appearing on the surface than winter spills. Quantitative measurements of oil are required.

Brown (1977) reported on a paper chromotographic technique wherein flourescent hydrocarbon, extracted from sediments, were concentrated. Spots appearing under UV light indicated the presence of hydrocarbons. Minimum detection limits were 2 mg of a mixed crude oil. By following his procedures a positive result would indicate at least .8 mg of oil was present in a liter of sediment and, through a modification, relative concentration in various portions of a site could be determined. The technique should be examined for use in terrestrial sites, since it resembles that developed by CRREL personnel, Deneke, et al. (1975). Brown (1977) suggested that n-butane may be preferred as a solvent in cold regions because it would evaporate faster than hexane during the concentration step in the procedure.

Perhaps the easiest method to quantify spill damages would be by gravimetrically measuring oil content of the soil. However, evaluations based only on oil weight could be inadequate. Both soil type and type of product spilled must be considered. According to McGill (1975), the amount of damage caused by oil spills is closely related to the amount of oil remaining in soil following initial clean-up operations. Thus, gravimetric extraction of oil would allow an initial assessment of the degree of damage.

Applying the gravimetric technique necessitates an understanding of

its limitations with respect to correlation with plant responses. Short, Rice, and Cheatum (1976) rejected gravimetric techniques for determining water-soluble toxic fractions of oil in marine habitats. They detected substantial volatilization of such compounds during the solvent evaporation step. Thus, gravimetrically determined oil content data for soils may be unreliable indices where volatile toxic fractions are important.

Schwendinger (1968) noted that the critical oil content of soil for plant survival was approximately 3% by weight. Above this concentration, plants showed severe damage symptoms. Udo and Fayemi (1975) observed a 50% reduction in corn germination at a 4.2% crude oil pollution level. Tentative guidelines suggested by McGill (1975) for Canadian conditions, indicate very severe plant damage can be expected on mineral soil containing greater than 5% crude oil by weight. Similar damage can be expected on organic soils with greater than 75% oil content. McGill and Nyborg (1975) found oil contents of the upper 4 cm of organic peat soils ranging to 200% and 300%. In the 4-15 cm layer, maximum contents were about 35% of the dry oil-free peat. McGill's guidelines indicated soil properties are vitally important in interpreting gravimetric data. Perhaps such data could be more easily interpreted in terms of plant effects if comparisons were made on a volume basis of soil rather than on a weight basis (discussed in detail later). Nevertheless, certain soil physical properties are important determinants affecting the impacts oil can have on plants.

Oil contamination of soil varies spatially in natural settings due to uneven topography. Micro habitats should be grouped according to

suspected oil contamination and subsamples collected separately. For example, a cotton grass tussock should be sampled separately from depressions between tussocks. Deneke, et al. (1975) observed that microrelief significantly affected the degree of plant damage following oil contamination. McGill and Nyborg (1975); and Walker, Everett, and Weber (1978) all reported differential oil penetration in soil which was related to apparently varying soil moisture levels. The subsamples should be thoroughly mixed perhaps by a kitchen blender or soil grinder and composite samples then taken for analysis.

Variability investigations and adequate sample sizes should be calculated prior to determining oil content of either soil or sediment, especially where data will be used for research purposes. Without such information, significant time and resources can be expended, acquiring unreliable data.

Cook and Westlake (1973) experienced a lack of reproducibility and sensitivity in using the gravimetric procedure. The net weight of extracted oil may not be due solely to oil evaporation and degradation, but may reflect weight gains by oxidation (Zobell, 1973).

Nevertheless, if details of change in specific components is not required, gravimetric extraction provides a good technique especially useful when many samples are to be processed.

Crude oil is a very complex natural organic product whose components range in molecular weight from 16 (methane) to well above 20,000. Thompson, et al. (1971) released information pertaining to the general characteristics of the Prudhoe Bay crude oil. Structurally, the compounds in oil include saturated straight and branched chains, sat-

urated and aromatic rings, and hetero-compounds containing N, S, O, metals, and other various additions. Gravimetric oil analysis has the attraction of simplicity, and many authors have extracted oil from soil, but, unfortunately, no standardized solvent or extraction procedure has been uniformly accepted. Baldwin (1922) extracted oil from soil using equal parts petroleum ether and diethylether; these solvents also were later used by Dobson and Wilson (1964). Alkane solvents have been employed by several workers. Cook and Westlake (1974) used pentane, and hexane has been used by Jones (1969), Gudin and Syratt (1975), and Swader (1975).

Other workers have extracted oil using several of the short-chained, chlorinated hydrocarbons: Ahlfeld and LaRock (1973) chloroform-methanol, 3:1, Rowell (1975) methylene dichloride, Kincannon (1972) carbon tetrachloride, and Sellberg (1975) carbon tetrachloride. The zaeotrope benzene-methanol was used by Duffy, et al. (1975) (3:1), Giger and Blumer (1974) (3 2/3:1), and Pierce, Cundell, and Traxler (1974) (60:40 in 0.1N KOH). In their field test procedure, Deneke, et al. (1975) extracted oil from soil using cyclohexane.

CONCAWE (1972) outlined two methods for extracting hydrocarbons from soil. The first was a carbon tetrachloride elution with the eluate passing through a mixture of Florisil and "alumina acidic" to remove non-hydrocarbons desolved from the soil. The second method was a steam distillation process that reportedly removed hydrocarbons with B.P. about 400 C. Neither method appeared well-adapted to rapid and routine testing of large numbers of soil samples. Vanloocke, et al. (1975) suggested that soils be dried with Na_2SO_4 prior to extracting with

either hexane or carbon tetrachloride.

Typical extraction procedures consisted of placing 20-50 g oiled soil into a Soxhlet apparatus and refluxing for 16 hr with 220 ml of a 3:1 mixture of benzene:methanol (Duffy, et al. 1975). Extracted residues can then be weighed following solvent evaporation under N2.

Extractions probably vary substantially among techniques and experiments due to the range of polarities among solvents and soil contaminants. Furthermore, the soil organic matter may contain molecular structures similar to certain of the crude oil fractions. Many soils in the Arctic and subarctic have thick highly-organic surface mats, unlike soils in warmer regions. Each solvent removes specific fractions of the organic soil components, which would bias estimates of oil. Blumer and Youngblood (1972) observed soils to commonly contain polycyclic aromatic hydrocarbons. They speculated that these compounds were formed by natural fires. Because wild fire is common to the interior of Alaska, there may be a reservoir polycyclic aromatic hydrocarbons in those soils. Apparently, that has not been investigated.

A systematic survey is needed to evaluate the efficacy of oil-extracting solvents and extracting procedures to delineate those methods which extract various oil components in an unaltered state which, at the same time, do not solubilize soil organic fractions. Perhaps one or several of the methods recently proposed for marine sediments (Farrington and Tripp, 1975) may have application in terrestrial, arctic ecosystems. These methods need evaluation under field conditions in the far north. Just as important as the actual oil content on a spill site is an interpretation of what the value means. For example, what are the ecological

and biological implications if the soil contains 3, 5, or 10% oil? What are the critical oil content levels for various soil fauna and flora? What site factors modify the critical levels? Zobell (1973) noted that only by the standardization of testing procedures and the standardization of units of expression will it be possible to compare results obtained among various laboratories.

After soil extraction, many workers further subdivide the oil residue into various components. Elution during liquid chromatography through a deactivated silica gel column overlaid with deactivated alumina is commonly used (Cook and Westlake, 1973; Farrington and Tripp, 1975; Blumer, et al., 1972; and Morgan, 1975). Silica gel is used because it separated saturated and aromatic hydrocarbons well. The short alumina bed on top of the silica gel retains the polar, high molecular weight materials for which silica gel has only a limited holding capacity (Blumer, et al., 1972). Morgan (1975) suggested column preparation by heating 60-200 mesh silica gel at 120° C for 18 hr and then deactivating each by the addition of 5% water (weight to weight) prior to column packing.

The chromatographic technique as suggested by Cook and Westlake (1973) resolved crude oil into asphaltene, saturate, aromatic, and NSO fractions. Results were expressed gravimetrically and provided a reliable index to macro-changes in oil composition. The oil fractions were defined according to the method of separation. Cook and Westlake (1974) observed reductions in saturate and aromatic components and increases in quantities of asphaltenes as microbial growth occurred. The NSO fractions also altered microbial activities but in a random

manner. They were unable to relate bacterial populations to specific changes in chemical composition of the various crude oils in their study.

Gas chromatography is a useful technique for following changes in the composition of the N-alkanes. N-alkanes are believed to be among the first crude oil components to volatilize and to be microbially degraded. Thus, their losses signal initiation of the natural recovery process at a spill site. That information is valuable, but it must be remembered that N-alkanes constitute only one fraction of crude oil hydrocarbons. Unless concerned solely with the degradation of this labile oil component, the usefulness of gas chromatography is limited. Furthermore, a gas chromatograph-mass spectrometer process is needed to positively identify various oil compounds identification. Other methods of oil component identification include infrared and flourescence spectrometry.

It should be noted that recent evidence reported by Sexstone, et al. (1978) suggested that hydrocarbon classes in oil spilled on tundra soils at Barrow did not change over time. That finding indicated under those conditions degradation occurred across all hydrocarbon classes simultaneously. Thus, some question remains concerning oil degradation and utility of the N-alkanes as indicators of biological degradation, at least with respect to cold-region soils.

Deneke, et al. (1975) discussed a semiquantitative field technique, based on flourescence of certain crude oil components. The technique was capable of detecting the presence of petroleum products in soil and water. Various components present in crude oil, and in most petroleum

products, flouresce when exposed to ultraviolet light. Peake, et al. (1975) determined that water-soluble components in crude oil responsible for florescence were mainly naphtahlene and alkylated derivatives. During the weathering process of oil in the natural environment, florescent properties may change. Mackay, et al. (1974) suggested that the monitoring of water-soluble aromatics would be a tractable method to characterize crude oils. Short, Rice, and Cheatum (1976) favored infrared spectrocopy for quantifying water-soluble fraction of Alaskan crude oils.

After reviewing various techniques for measuring oil content of soils, Vanloocke, et al. (1975) concluded that, "the quantitative measurement of hydrocarbons in soil is difficult and approximative". Our review indicates there has been no substantial developments since, which would alter those observations. The most precise technology involves extracting the hydrocarbons, separating them into various chemical groups and then quantitatively analyzing each group. Due to chemical property distinction among groups of hydrocarbons, a variety of instruments is needed to measure each quantitatively. Most Alaskan ecological research groups involved with environmental assessments of oil pollution have been neither equipped nor staffed to adequately address that problem. Consequently, they have had to use the instruments and technology within their means whether or not it was best suited for the particular work. Oil spill ecological research in Alaska has usually lacked petroleum chemists. Oil spill research in Alaska needs more cooperation among scientific disciplines and groups to enhance various project accomplishments.

Ideally, the petroleum chemists ought to be providing the biological and environmental scientists with quantitative data. Such cooperation was noted among temporate-zone researchers at the 1975 Conference on Prevention and Control of Oil Pollution (25-27 March 1975, San Francisco, California). Much of the oil spill research in Alaska has only recently progressed to that point by efforts from the University of Louisville group. There are at least three Alaskan laboratories which have reported data for oil pollution measurements: 1) the Institute of Marine Science and Arctic Environmental Research Laboratories at Fairbanks, 2) the Agricultural Experiment Station Laboratory at Palmer, and 3) the National Marine Fisheries Service Auke Bay Laboratory at Auke Bay. The Institute of Marine Sciences Laboratory is possibly the best in terms of staff expertise and equipment in Alaska, particularly for measuring pollutants in water. The Agricultural Experiment Station Laboratory is possibly the only one that has been used for soil sample analyses, although the Arctic Environmental Research Laboratory is responsible for data from the current experimental spill studies near Fairbanks. There are facilities outside Alaska, which have been used by CRREL, University of Louisville, UPI, Ohio State, and University of Colorado scientists.

Oil Movement in Soil

The direction of oil flow from a spill site and the shape of the spill area are primarily controlled by topography. Mackay, et al. (1975) noted that oil will flow downhill, spreading over the surface and penetrating vertically into the soil until groundwater, an impervious layer of clay or rock, or the frost level is reached. In arctic and subarctic regions, the extent of coverage is heavily dependent upon the presence and state

of an organic mat. An organic mat saturated with water and frozen will allow little oil penetration, and the size of the spill area will increase as oil flows over the surface. However, with a thick organic mat and deep active layer significant quantities of oil can be retained, reducing spatical distribution of the oil (Collins, et al., 1978).

Mackay, et al. (1974) observed near Norman Wells in the Northwest Territories that the moss layer becomes explosively flammable when first impregnated with crude oil. However, summer evaporation of Norman Wells crude oil was very rapid with up to 40% of the oil being volatized in one day. Typically, the vapor pressure of hydrocarbons dropped by a factor of approximately four as the temperature fell from 70 to 32° F.

Perhaps the most complete analysis presently available on the physical movement of oil in soil is the discussion by Somers (1974). He separated oil transport in soil into: 1) multiple phase flow, and 2) single phase flow. The multiple phase flow described water unsaturated soil conditions in which the oil was free to flow intact through the soil matrix; whereas the single phase flow described conditions in which the soil pore space was filled with water and only water-soluble hydrocarbons were free to infiltrate.

Mackay (1975) speculated that subsurface oil, shielded from atmospheric turbulence and isolated by the presence of an overlying organic mat, had a much reduced weathering rate, perhaps by a factor of 10^2 to 10^3, and as a result, more volatile components of crude oil would be retained. Field core isoprenoid ratios revealed, furthermore, that biodegradation rates decrease with depth, presumably due to reduced oxygen availabilities (Duffy, et al., 1975). Observations by Deneke, et

al. (1975) on permafrost slopes of interior Alaska suggested that once crude oil percolated through the soil profile and reached the zone of maximum soil saturation, or permafrost interface, it would move laterally downslope with no significant movement upward into the drier moss layer. Thus, oil may contaminate areas adjacent to spill sites and not be detected by visual surface inspection, which is precisely what was observed in the Fairbanks test (Collins, et al., 1978).

Oil spills on land have the potential of long-term threats to ground water quality as demonstrated by Duffy, et al. (1975) and Vanloocke, et al. (1975). Little is known concerning solubility of hydrocarbons in practical situations especially under cold-dominated environments. Partial oxidation of insoluble or slightly soluble oil compounds may result in the formation of more soluble components which then are free to migrate with soil water (Duffy, et al., 1975; Somers, 1974). The consequences of this are unknown with respect to permafrost interfaces. In terms of ground water pollution, Atlas (1977) recently reported on stimulating biodegradation of oil and noted that a technique of aerating and fertilizing a gasoline-contaminated ground water reservoir in the literature. That approach was the only successful report we found. During the seasonal freeze-thaw cycle, will oil or water-soluble oil components penetrate permafrost or ground ice? If this occurred, what would be the long-term implications? Raymond, Hudson, and Jamison (1976) found no losses of oil from treated plots in either runoff of oil and water-soluble oil components in cold-dominated environments.

Microbial Degradation of Oil in Cold Soils

As discussed by Deneke, et al. (1975), the natural rehabilitation

of oil contaminated sites is slow in arctic and subarctic regions. Four natural pathways exist for spilled-oil removal; these include evaporation, leaching, chemical oxidation, and biological oxidation. Perhaps the process currently receiving the most attention as a means of accelerating natural recovery is biological oxidation. Mackay, Charles, and Phillips (1975) reported that microbial oxidation would probably dominate oil decomposition losses two years after oil contamination because other processes would have declined in effectiveness by then. Sexstone, et al. (1978a) reported persistence of spill hydrocarbons in arctic tundra soils 28 years following the spill, suggesting the slowness in which biological degradation occurs in the Arctic. But Sexstone, et al. (1978b) indicated biological degradation was occuring in arctic soils, even though there was little preferential degrading of structural classes of petroleum compounds.

It must be remembered that net biological oxidation can be extremely slow in certain microhabitats of cold regions, as evidenced by the recent discovery of an ancient human corpse in Western Alaska, and the discoveries of rhinocerous and mammoth remains in Siberia (Tolmachoff, 1929) and 8300-year old marine fossils including their soft parts in Greenland (original documents cited by Nichols, 1961).

In the biological treatment of soil contaminated with petroleum products, microorganisms play the dominant role in the decomposition process. Numerous genera representing bacteria, filamentous fungi, yeasts, and actinomycetes are reported to be active in oil degradation. In a review of literature, Ellis and Adams (1961) stated that prior to 1961, 100 species of organisms representing 31 genera had been identified which were capable of degrading crude oil and various oil products.

Information pertaining specifically to cold-dominated soils is scarce.

Knowledge of these organisms and their interaction with oiled soils, especially under extreme northern climatic conditions, should be understood to promote rapid rehabilitation of oil-soaked soils. However, Atlas (1977), who is a leading authority on this subject noted the biodegradation of oil is a complex problem and the most successful approach appears to be modifying the environment to stimulate the organism. Attempts at changing the microbial population through inoculation, etc., have more severe constraints and, consequently, less probability of success than processes that would stimulate natural populations.

Parkinson, Gossen, and Henderson (1975) reported that although microbial populations shifted following an oil spill, total microbial biomass was little affected; however, they observed that in their field trials a considerable reduction in cellulose decomposition followed oil additions. A number of fungal species capable of metabolizing a wide range of n-alkanes in crude oil were identified. A viable fungal component existed at two acidic, oil contaminated sites in the MacKenzie Delta, (Parkinson, 1973). Scarborough and Flanagan (1973) reported that the addition of oil to the arctic environment consistently yielded increased numbers of filamentous fungi and yeasts, however, the diversity of species decreased. Atlas, et al. (1976) noted that microbial populations were markedly different near a natural oil seep at Cape Simpson, Alaska, compared with surrounding areas. The seep was devoid in some areas of bacteria, but in the bacteria-free areas, abundant fungi were found.

Cook and Westlake (1973) reported the application of crude oil had no effect on numbers of fungi in soil although bacterial populations greatly increased. Similar observations were made by Babb and Bliss (1974) on Devon Island after adding diesel fuel. Campbell, Harris, and Benoit (1973) reported the predominant organisms on oil-spill sites at Barrow, Alaska were members of the bacterial genera Pseudomonas and Achromobacterium. Similarly, Cundell and Traxler (1974) isolated Pseudomonas, Brevibactcerium, Spirillum, Xanthomonas, Alcohgenes, and Arthrobacter from a natural arctic oil seep. They considered the majority of these isolates to be psychrotolerant and not obligate psychrophiles.

At some northern locations the fungal component appears to dominate in the degradation process of oil while at other sites bacteria are important. Perhaps soil environmental conditions, more specifically soil pH, is a contributing factor, with the fungi being more prevalent at low pH's and the bacteria at near neutral pH's. Cook and Westlake (1974), by the addition of lime, significantly increased the bacterial population on acid soils receiving crude oil.

The population response of specific soil organisms to added oil may be: 1) decrease in numbers due to toxic effects of the oil, 2) decrease in numbers due to competition for organic growth factors or inorganic nutrients, 3) decrease or increase in number due to physical alteration of the soil environment; reduced oxygen tension, increased temperature, etc., and 4) increase in numbers due to increased energy and carbon sources from: a) the hydrocarbons themselves, b) secondary oxidization products of hydrocarbon metabolism, and c) biota protoplasm from oil-

destroyed microorganisms, fauna, and plant tissue. A change in population of a specific organism following oil application to soil does not necessarily indicate a toxic or stimulatory effect of the oil, per se, but simply reflects a change in soil conditions. Sparrow, Davenport, and Gordon (1978) reported extensive data on population responses by soil microbes in different soil horizons following oil spillage onto an interior Alaskan forest site near Fairbanks.

Fertilizer Additions

Crude oil is a highly carbonaceous material low in inorganic minerals. When added to soil, microorganisms oxidize a portion of the carbon for energy and incorporate a portion of the carbon into microbial protoplasm. In the formation of new microbial tissue, mineral nutrients including N, P, K, Mg, Ca, etc., are required. The soil is the source of most of these elements. If the soil cannot provide the elements rapidly enough to satisfy the microbial demand, mineral nutrients limit the rate of oil degradation. Eventually, as microorganisms die and their bodies decompose, the mineral components will be recycled into new organisms requiring energy, which in turn required further oxidation of hydrocarbons. This may be a slow process, in the natural environment, possibly requiring several years.

Vestal, et al. (1978) reported that oliophilic phosphorus increased the microfloral populations of oil-affected arctic ponds. They concluded that containment and phosphorus fertilization may be a reasonable approach to stimulate biological degradation of oil in arctic ponds. The use of oliophilic fertilizers had been previously tested in the arctic, according to Atlas, et al. (1977).

After reviewing the international literature on hydrocarbons decomposition in soils, Vanloocke, et al. (1975) concluded: "Recent advances in this regard indicate that the time required for microbial clean-up (sic) be reduced from several decades to a few months by the enhancement of the microbial biodegradation process through the optimalization of the nutrient balances of the soil".

If suitable electron acceptors and growth factors are present, the addition of fertilizer to most soils will increase the rate of microbial breakdown of oil. Schwendinger (1968) noted that fertilizer increased microbial activity. Urea phosphate added to oil-soaked soil increased bacterial numbers and rate of disappearance of n-alkanes (Cook and Westlake, 1973). Hunt, et al. (1973) noted microbial activity and density of vegetation increased with fertilizer additions. Rowell (1975) observed that cultivating and adding N, P, K, and S resulted in increased microbial degradation. Atlas and Bartha (1973) stated that biodegradation of oil at sea is seriously limited by the scarcity of nitrogen and phosphorus. These and other investigators agree upon the stimulatory effects of added fertilizer.

Following oil contamination of soil, the nutrient most likely limiting microbial development is nitrogen. Campbell, Harris, and Benoit (1973) at Barrow, Alaska obtained bacterial counts 12 times greater on fertilized than unfertilized, oiled plots. The exact fertilizer treatment was not specified. They further observed an increased incidence of Azotobacter sp. with enhanced nitrogen fixing potential in oiled plots. This is in agreement with literature for temperate regions. Research is needed on methods of enhancing nitrogen-fixation in oil

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polluted soils in the far North; stimulatory modifications of the environment, if any, such as added mineral nutrients, growth factors, etc., which favor development of free-living, N-fixing organisms should be identified.

Gudin and Syratt (1975) described observations from 15 oil contaminated sites in the United Kingdom. Their survey indicated that plant species of the Leguminosae family are abundant in oil contaminated areas, possibly due to the N-fixing symbiotic relationship with Rhizobium sp. Eight leguminous species representing four genera; (Astragalus, Oxytropis, Hedysarum, and Lupinus), have been identified and found to be profusely nodulated in the Barrow-Umiat regions of Alaska. These were growing in permafrost soils with 10-20" active layers (Allen, et al. 1963). The tolerance of these species to oil is unknown as is their potential for revegetation on oil contaminated sites. Additionally, Alnus sp. is a common N-fixing shrub in Alaska. We do not know if this species will fix nitrogen in oiled soils. Symbiotic or nonsymbiotic N-fixation of oiled sites is appealing from two standpoints: 1) it is a "natural" technique for oil-spill reclamation and may be less costly in the long term than fertilization, and 2) the biological addition of nitrogen, in general, is a self-limiting process in that as the quantities of available nitrogen increase in the soil the efficacy of N-fixing organisms decrease (Alexander, 1961); hence, reaching toxicity levels of soil nitrogen is not a risk.

Nyborg and McGill (1975) concluded that periodic nitrogen application with annual quantities totaling more than 500 lb per acre may be required for a 2- to 3-year period following a spill. Soil respiration

in a laboratory study involving oiled soil, although greatly increased by nitrogen fertilization, was insensitive to nitrogen source, i.e., the ammonium and nitrate forms both were equally effective (Deneke, et al., 1975). However, in field situations the effectiveness of one N-source versus the other has not been clearly demonstrated. In wet soils, the anionic form (NO_3) may be free to diffuse or leach into neighboring non-oiled areas, while the cationic ($NH+_4$) form may be immobilized on the exchange complex. Furthermore, Taylor, et al. (1970) isolated a Pseudomonas sp., a common oil-decomposing genus in soil (Babb and Bliss 1974), that was capable of anaerobic growth on aromatic compounds by nitrate respiration. Little field data exists on leaching and denitrification of nitrate-nitrogen added to oiled soil, especially in arctic and subarctic regions. Nyborg and McGill (1975) warned that heavy application of ammonium-based fertilizer should not be used on oil spills unless lime was added to prevent a reduction in soil pH. However, care is needed to avoid over-application of lime added with NH_4+ based fertilizers as NH_3 volatilization could result.

McKendrick and Mitchell (1978a) found phosphorus fertilization was essential to the establishment of grass seedlings on an oil-damaged wet tundra site at Prudhoe Bay. Furthermore, the presence of phosphorus stimulated the natural reinvasion of mosses which had been eliminated by the spill. How this treatment affected oil decomposition is yet unknown.

Over-fertilization of a spill site could result in ground and surface water contamination. Also, over-fertilization with various forms of fertilizers will increase osmotic potentials of the soil

solution which might be detrimental to both microorganisms and higher plants. Further work is needed to define the quantity and composition of fertilizer required at a spill site and to determine how this varies with soil conditions, quantity of oil spilled, type of oil, and climatic conditions. Nitrogen added to an oil spill and assimilated by microbes will be eventually mineralized from the microbial biomass and soil humus. Under such conditions, it appears that higher plants should be reestablished to promote nutrient recycling within the ecosystem and to prevent eutrophication of surface waters.

One approach for determining fertilizer requirements is to periodically test the soil and to add fertilizer only when deficiencies are indicated (McGill, 1975; Rowell, 1975; Westlake and Cook, 1975). Kincannon (1972) tested soil monthly for ammonium and nitrate. He fertilized with ammonium nitrate (33-0-0) to maintain 10-50 ppm mineral nitrogen level in the soil solution. Appropriate soil test levels and extracting solutions to monitor oil degradation are poorly enunciated: For Alaska, and possibly other cold regions, none are available. The interpretation of critical levels may be different for plant growth than for microorganism development. Traditional soil tests (especially for phosphorus and potassium) do not indicate nutrients which are immediately available in the soil solution but rather indicate nutrient levels which may become available to growing plants over a period of time. Perhaps the use of saturated soil extracts (SSE) would be appropriate in evaluating nutrient requirements during oil degradation. In this procedure, the soil solution is removed from solid matrix under vacuum filtration and analyzed directly for nutrients (U.S. Salinity

Laboratory Staff, 1954). This should indicate nutrients readily available to microorganisms.

A further consideration in using soil testing to guide fertilization is that oiled soils possess hydrophobic properties. Thus, during nutrient extraction, the center of hydrophobic aggregates are not uniformly wetted with the solution; hence, the higher the oil content of soil, presumably the lower the soil test levels. Everett (1978) observed that in tundra soils from Barrow, Alaska. E. J. Udo (University of Ibadan, Nigeria, personal communication) noted that cation exchange capacity (CEC) seemed to decrease with an increase in the pollution level. Similarly, Kincannon (1972) determined that the CEC increased during the course of his study, which possibly was related to the decrease in oil content due to microbial degradation with time. Soil testing as influenced by the oil content in soil should be a fruitful area for future research.

Microbial Inoculation

A preliminary survey of MacKenzie Valley soils for oil decomposing organisms indicated that such activity was not uniformly found among the indigenous microflora (Cook and Westlake, 1973). However, a following study concluded that all samples analyzed from the MacKenzie Valley area contained microorganisms capable of limited growth on Prudhoe Bay crude oil (Cook and Westlake, 1974). These researchers were unable to stimulate oil degradation under field conditions by seeding with oil-utilizing bacteria. Atlas (1974) analyzed selected Alaskan waters and determined all contained microorganisms capable of oil biodegradation. Jobson, et al. (1974) stated that the application of oil-utilizing bacteria

resulted only in a slightly accelerated rate of utilization of n-alkane components of crude oil.

Hunt, et al. (1973) reported that a positive response obtained by bacterial inoculation of Fairbanks silt loam was unexpected since organisms capable of degrading oil were normally present in that soil type. They reasoned the positive response was related to the generation time of the microorganisms in their experiment conducted at 15° C. Schwendinger (1968) noted an increased rate of carbon dioxide evolution due to bacterial seeding in his laboratory study. Miget (1973) reported some degree of success in stimulating oil utilization under simulated field conditions through microbial seeding.

Rowell (1975) observed a lag time with most soils after the addition of oil before an active oil-decomposing population became established. He attributed this lag to the period required for organisms to synthesize enzymes (adaptive enzymes) needed to utilize hydrocarbon components. Presumably, the lag time is a function of temperature, because lag times increased with a decrease in temperature. Mulkins-Phillips and Stewart (1975) in working with oil degradation in a marine environment observed that a Nocardia sp. averaged a 2.2-fold increase in generation time with a 10° C decrease in temperature.

One alternative in reducing adaptation time of indigenous microorganisms would be to culture the organisms in the laboratory on an oil substrate until they were in their logarithmic growth stage and then introduce them into the contaminated soil. Furthermore, if a mixture of proven oil-decomposer was used, species may be added which were not part of the indigenous soil population and these organisms may enhance the

total degradation process. Cook and Westlake (1974) noted in their survey that inoculates from soil samples obtained at specific locations varied considerably in ability to utilize Prudhoe Bay crude oil. From the literature, it appears that most single organisms do not have enzymatic capabilities to metabolize all components of spilled oil; thus, a mixed culture would be highly desirable (Miget, 1973). Parkinson, Gossen, and Henderson (1975) stated that many of the oil-degrading bacteria appeared to be selective in the range of n-alkine utilization; however, the fungi were capable of utilizing a wider range of n-alkanes. Parkinson (1974) indicated that more species of bacteria than fungi appeared capable of metabolizing crude oil. Also, because they have a more rapid generation time, the bacteria are usually considered for oil-spill inoculation.

Microbial seeding requires adapted cultures. Two procedures are available for mixed-culture formation. The first is to grow the individual organisms separately and combine them prior to soil inoculation. The second consists of an enrichment technique in which suitable soil is enriched with crude oil and this is used for inoculating soils at a spill site. Cook and Westlake (1973) have determined that the source of crude oil and the temperature are important in the incubation process. Organisms should be grown on crude oil of compatible quality to that at the spill site. Further, populations enriched at 4° C utilized the same oil at 30° C, but those enriched at 30° C could not uniformly grow at 4° C. Thus, for cold-dominated sites, innoculums should be organisms that were grown in the laboratory under psychrophilic conditions.

Westlake and Cook (1975) warned that artificially introduced micro-

organisms may be pathogenic or toxic to man. This possibility should be fully evaluated before indiscriminately using soil inoculation for oil spills.

Lehtomaki and Niemela (1975) reported in Finland that adding pure cultures to soil did not statistically influence oil concentration; however, adding brewery waste yeast accelerated the oil degradation rate two- to ten-fold. Neither irrigation, fertilization, nor aeration proved equally effective as the addition of waste yeast in accelerating oil decomposition. They concluded that yeast presumably provided useful nutrients or growth factors for microorganisms cometabolizing oil in soil. This study strongly indicates additional work involving possible growth factors, from sources such as brewery waste yeast, should be pursued.

Deneke, et al. (1975) concluded that recent experiments in microbe-oil relationships indicate microbial seeding combined with fertilization has definite possibilities in arctic regions. Field work is needed at a number of locations under a variety of environmental conditions to either verify or disprove the use of microbial inoculation in oil spill restoration.

Aeration

Crude oil has a high carbon and hydrogen content but is quite low in combined oxygen. Breakdown proceeds most rapidly by an oxidative process, either chemical or biological. Parkinson (1974) demonstrated, however, that anaerobic degradation may occur in waterlogged soil, although at a much reduced rate compared with aerobic degradation. One of the suspected effects of adding large quantities of oil to soil is to

change aerobic conditions to anerobic conditions because of the high biological oxygen demand. In this regard, oil would not only contaminate soil, but also prevent its own degradation. Furthermore, crude oil spilled over the surface of soil, especially in wet sites, can form a relatively impermeable barrier, reducing gaseous exchange between the soil and atmosphere (Parkinson, 1974).

Hoeks (1972), near a natural gas pipeline leak, found low oxygen content in the soil air. He attributed this to: 1) displaced soil air by leaking gas, and 2) increased oxygen consumption resulting from methane oxidation. He concluded, where an excess of methane was present, that the rate of oxidation of methane depended solely upon the rate of oxygen supply. Similarly, Johnston (1970) concluded that breakdown of crude oil residues in a sand culture was dominated primarily by oxygen availability. Also, it was shown by Blumer and Sass (1972) that the hydrocarbon degradation rates in sediments decreased with increasing depth. These studies signify the importance of free-molecular oxygen in the breakdown process of oil. Readers interested in O_2 values for oiled arctic ponds should examine the report by Vestal, et al., 1978.

When free-molecular oxygen becomes limiting in soil, alternate terminal electron acceptors are required. Redox potentials indicate nitrate serves as the next electron acceptor, being reduced to nitrogen oxides and nitrogen gas. Upon further reduction, ferric and manganic ions are reduced. Ellis and Adams (1961) and Udo (1975) considered the increase in manganous ions, produced by reducing conditions in the presence of crude oil, as the prime factor responsible for decreased plant growth in oil contaminated soils. Elliott and Blalock (1975)

showed that large quantities of plant residue in soil also increased soluble manganese. Thus, if the toxicity of manganese is discovered as a cause of plant death in oil contaminated soils, it may have resulted from the high oxygen demand of the crude oil and not by any inherent properties of the oil itself.

In closed systems when free-molecular oxygen becomes limiting, the general tendency is for end products to be only partially oxidized. Thus, during hydrocarbon oxidation with limited oxygen, presumably hydroxyl, carboxyl, and other partially oxygenated compounds will be formed. Kincannon (1972) noted an increase in organic acids in soil during oil decomposition. These forms may be more water soluble, hence, more damaging, in ground and surface water than the original constitutes of crude oil.

Cultivation is one means suggested for increasing aeration in oiled soils (Dobson and Wilson, 1964; Kincannon, 1972; Dotson, et al., 1971). In colder soils, Rowell (1975) noted an increased rate of vegetation recovery of oiled soils due to cultivation. Westlake and Cook (1975) observed no increased rate of microbial oil utilization with cultivation. The effect of cultivation on volatility of hydrocarbons versus increased incorporation of oxygen into the soil should be studied independently; however, both tend to simultaneously remove hydrocarbons from the soil environment.

Degradation of Oil Fractions

It is generally believed that the components of crude oil most susceptible to biodegradation are the normal (straight chain) paraffinic hydrocarbons (n-alkanes). Branched-chained paraffins and cycloparaffins

are decomposed somewhat more slowly. Many of the aromatic hydrocarbons and non-hydrocarbon compounds, particularly those of high molecular weight, are decomposed very slowly. Kator (1973) noted that microbial utilization rates were inversely related to chain length. However, as cited above, recent evidence presented by Sexstone, et al. (1978) suggests that in natural soils of the Alaskan Arctic, degradation may occur uniformly among hydrocarbon classes. There is need to resolve such findings.

The rate and degree of utilization under similar conditions of crude oils from diverse origins is not constant (Cook and Westlake, 1974; Rowell, 1975; Atlas, et al., 1976); but varies from oil to oil. However, Westlake, et al. (1974) reported only limited success in relating chemical properties and composition of crude oil to its rate of decomposition.

Cook and Westlake (1974) noted, along with numerous other workers, that fertilization increased utilization of n-alkanes. Further, they noted that the isoprenoids, phytane, and pristane, were more resistant to microbiological attack but were eventually degraded. Phytane and pristane were utilized at different rates in different oils under psychrophilic conditions. Thus, as Cook and Westlake (1974) pointed out, the usefulness of rate of removal of these compounds for determining degree of oil degradation in natural environments as some authors have done is limited.

The quality or composition of oil also has an effect on the utilization capability of microbial inoculates (Cook and Westlake, 1974). Populations obtained on poor quality oil (low in n-alkanes) readily metabolized higher quality oil; however, enrichments obtained on high

quality oil had only limited ability to metabolize low quality oil. Traxler (1973) also noted that aromatic hydrocarbon-utilizing bacteria were able to grow on alphatic hydrocarbons but the reverse was not necessarily true.

Many crude oil fractions are subject to degradation, even under the psychrophilic conditions of arctic and subarctic regions. However, degradation rates of specific components of crude oil under cold conditions still warrant further investigation. Westlake and Cook (1975) suggested that since sufficient differences exist in the biodegradation of various crude oils, that the oils to be transported in the Arctic and subarctic should be individually tested in the laboratory prior to movement in the field. This information on rate of decomposition of various crude oils under cold conditions might assist in developing arctic restoration programs for use following an accidental oil spill.

Though the short-chained alkanes are the fractions most easily volatilized and most easily metabolized, environmental conditions may prevent their losses following a spill. With deeper penetration of crude or fuel oil into the soil, gaseous exchange, including losses of volatile hydrocarbons, is reduced. Deneke, et al. (1975) observed that 15 years after a gasoline spill at Milepost 382.5 on the Haines-Fairbanks pipeline, soil pits still had a strong odor of petroleum.

Special forms of tillage may be helpful in reducing fuel concentrations deep in soil profiles by: 1) increasing hydrocarbon evaporation, and 2) increasing oxygen incorporation into the soil. Where permafrost occurs, these methods may not be appropriate.

Temperature Effects

Bacteria are capable of utilizing crude oil under field and

laboratory conditions at 4° C. In the marine environment, ZoBell (1973) reported microorganisms were able to degrade crude oil at -1.1° C. Although hydrocarbon degradation occurs at temperatures approaching freezing, microbial growth rates increase with increasing temperatures. Mulkins-Phillips and Stewart (1975) in a laboratory study on various petroleum products, observed an average 2.2-fold decrease in generation time with a temperature increase from 5 to 15° C.

In arctic and subarctic regions, the time required for microbial degradation of spilled petroleum may be extremely long due to: 1) low soil temperatures, and 2) short summer seasons during which microbiological processes are active. Campbell, Harris, and Benoit (1973) reported under conditions at Barrow, Alaska, that hydrocarbon decomposition was possible from late May until October. These workers further observed that the microbial response to crude oil was slow, with populations increasing one month after application; however, requiring as long as a second growing season to reach maximum numbers. If the cessation of microbial degradation after two years as reported by Sexstone, et al. (1978b) is a common phenomenon in the Arctic, there is a critical need to identify the cause of that and to pursue longer-term microbial studies. For the same reason, environmental recovery in the Arctic and subarctic may benefit from bacterial inoculation of petroleum-contaminated spill sites. Atlas and Bartha (1972) found that in addition to lowering biodegradation rates, low temperatures in marine environments caused long lag periods due to retention of volatile inhibitors in crude oil. It is reasonable to assume similar circumstances occur in terrestrial ecosystems.

Field studies by Parkinson (1973) indicated topographic differences influencing soil temperature significantly affected microbial degradation of crude oil. The preliminary results indicated respiratory rates in south-facing hummock slopes were approximately twice as great as in north-facing slopes. When the oil was extracted and analyzed using gas-liquid chromatography, the entire range of n-alkanes had disappeared from the south-facing slopes while little degradation of the oil had occurred in the north-facing slopes.

In an attempt to warm winter soils, Gudin and Syratt (1975) covered an experimental area with black plastic. They reported an increased rate of disappearance of waxy cake which had been incorporated into the soil. Dinkel (1966) reported polyethylene mulches to be effective in increasing soil temperatures near Palmer, Alaska. Clear polyethylene was more effective than black polyethylene. On spill sites in northern latitudes where in situ reclamation procedures are required, the use of clear plastic mulches may increase soil temperatures and thus, aid microbial degradation of oil. The timing of plastic application may be important depending upon the permeability of the plastic to volatile hydrocarbons. Field methods on this technique deserve further investigation in the arctic.

Units of Measure

In describing certain conditions of an accidental or experimental oil spill, quantitative units of measure are needed. Without such capabilities, measuring oil spill intensities and oil degradation (disappearance) becomes impossible, as noted in the previous section. Table 1 contains the possible combinations of weight and volume measures

for both substance spilled and either soil or sediment affected. Volumes and weights are common parameters used in quantifying fluids and solids. The use of fluid depth in oil spill experiments is possibly an adaptation of weather monitoring technology (precipitation) and agricultural irrigation and watershed techniques. In instances of accidental terrestrial spills there are often available estimates of either a volume or weight of material spilled. The area affected and depth of penetration can usually be measured. Thus, volume/unit area, volume/unit volume and weight/unit area, and weight/unit volume are parameters most likely useful for physically describing spill intensities. Terrestrial oil spill experiments should be designed so that one can readily relate physically controlled conditions to those of accidental spills; otherwise, there is difficulty in interpreting and applying research findings. Table 2 shows a variety of units of measure that have been used in experimental oil applications. The volume/unit area appears to have been most commonly used for field experiments. Volume/unit volume, volume/unit weight were least popular and usually used for laboratory container experiments. Weight/unit area, weight/unit weight and fluid depth applications were intermediate in popularity. Table 3 shows a table used at the Alaska Agricultural Experiment Station to relate fluid depth to various volumes/unit area.

Table 4 shows the variety of units of measure that have been used in reporting oil contents of polluted soils and sediments. Weight/unit weight was the most popular, which undoubtedly weakens chances of relating oil disappearance and reclamation studies with accidental and experimental spill pollution rates which are measured generally as

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volume/unit area.

The variations of English and metric units used should also be noted in Tables 2 and 3. Some researchers have reported mixed units, e.g. barrels/ meter^2, liters/foot^2, and centimeters^3/gallon. Consistency within language systems should be the rule. The metric language should be followed, and authors wishing to present English units should do so parenthetically.

However, there are more serious but less obvious deficiencies. The first involves problems with soil bulk density variations, which are possibly at their extreme in cold-dominated climates. In cold climates, organic matter can accumulate, which increases soil pore spaces and reduces bulk densities often to less than unity. Temperate zone agricultural soils bulk densities generally range between 1.1-1.5. Bulk densities have been determined for very few of Alaska's soils. However, the USDA Soil Conservation Service Soil Survey Staff (1975) included bulk density data for three Alaskan soils, which ranged between .35 and .96 on an oven-dry basis. Determining the quantity of oil retained within a spill site for purposes of either damage assessment or monitoring mitigating treatments on samples of soil or sediment would be an extremely useful procedure. Extracting and weighing oil from polluted soil or sediment can be readily accomplished. Small volumes of pollutants could prove difficult to measure accurately, however. Relating either laboratory weight or pollutant volume data to field sites would necessitate sampling by either volume or area in the field, which would be very difficult in highly organic and boggy soils. For instance, in the Davis, et al. (1972) review they report that 0.7% and 3% oil contents

are respectively equivalent to 50 and 225 barrels per acre. However, those values may be meaningless when applied to northern soils having significantly different bulk density, assuming the above values were derived from mineral soils.

If bulk density data were acquired by investigators to relate soil weight to volume then laboratory analyses could be performed on a weight basis and results used to calculate pollutant contents of field sites. Since peaty soils commonly weigh 400,000 to 500,000 pounds per-acre-furrow slice, and mineral soils weigh 2,000,000 to 2,500,000 pounds per-acre-furrow slice (Buckman and Brady, 1960), relating laboratory data to the field without reliable bulk density estimates could result in errors as great as 625%. For example:

> Suppose in the laboratory oil content for a soil was determined as 4% (w/w) and actual bulk density of the peaty soil is 0.20. But there are no bulk density data available, so field data are calculated on the basis of an "average" mineral soil with a bulk density of 1.25.
>
> Calculations based on incorrect assumption:
>
> (4% oil) (2,500,000 lbs soil) = 100,000 lbs oil/acre
>
> Calculations based on correct data:
>
> (4% oil) (400,000 lbs soil) = 16,000 lbs oil/acre
> (100,000 ÷ 16,000) (100) = 625% error

A second source of confusion in reporting oil contents lies in the method of expressing (w/w) percentages. Soil scientists express moisture content of soil on the basis of:

> Weight of water held in soil ÷ (oven-dried soil weight) (100) = % water.

Close examination of Table 4 reveals that two Canadian reports (McGill, 1975 and Duffy, et al., 1975) contained oil percentage data on

the oven-dried soil basis. Hence, their data were calculated: Oil weight ÷ (oven-dried soil weight) (100) = % oil. However, personal correspondence has revealed that some scientists unaccustomed to standard soil moisture expressions use a different formula: Oil weight ÷ (gross weight of soil + oil) (100) = % oil. Table 5 shows the relative differences that can result between the two methods of calculating w/w percentages of oil over a range of oil contents. The soil technique allows oil percentages to exceed 100, showing that some soils could hold more than their own weight in either oil or moisture. Highly organic soils may hold two to three times their own weight in oil (McGill and Nyborg, 1975).

Regardless of the method used to calculate oil percentages in soils, authors should indicate which they used so that comparisons among investigators' data are valid.

TABLE 1. Listing of possible methods for describing oil application (spill) rates and oil quantities present in either an experimentally or accidentally impacted soil or sediment.

Fluid	Soil or Sediment
Volume	Unit area
Volume	Unit volume
Volume	Unit weight
Weight	Unit area
Weight	Unit volume
Weight	Unit weight
Fluid depth	Soil or sediment depth

TABLE 2. Selected listing of literature citation and corresponding units of measure used to depict oil application and spill rates for terrestrial (soil) oil pollution studies.

Literature Citation	Units of Measure
(Volume/unit volume)	
Carr (1919)	Centimeters^3/gallon
(Volume/unit area)	
Mackay, Charles, and Phillips (1974)	Gallons/foot^2
Lindholm and Norrell (1973)	Liters/foot^2
*Brown and West (1970)	Liters/meter^2
McCown, et al. (1973)	" "
Cook and Westlake (1974)	" "
Haag and Bliss (1974)	" "
Jobson, McLaughlin, Cook, and Westlake (1974)	" "
Mackay, et al. (1975)	" "
Hutchinson, Hellebust, and Telford (1976)	" "
Mackay and Mohtadi (1975)	Meters^3/meters^2
Mackay, Charles, and Phillips (1975)	" "
Jensen (1975)	" "
Wardley-Smith (1976)	" "
Linden and Muller (1963)	Liters/hectare
Westlake and Cook (1975)	Kiloliters/hectare
Mackay and Mohtadi (1975)	Barrels/foot^2
Mackay and Mohtadi (1975)	Barrels/meter^2
American Petroleum Institute (1972)	Barrels/acre
(Volume/unit weight)	
McCown and Deneke (1973)	Percent (v/w)
(Weight/unit area)	
Rowell (1975)	Kilograms/meter^2
Gudin and Syratt (1975)	Kilograms/hectare
McGill (1975)	" "
Nyborg and McGill (1975)	" "
Nyborg and McGill (1975)	Pounds/acre
(Weight/unit weight)	
Plice (1948)	Percent (w/w)
Belyakova (1955)	"
American Petroleum Institute (1972)	"
Blumer and Sass (1972)	(pp 100t) Miligrams/100 grams
(Fluid Depth)	
**Gossen (1973)	Centimeters
Wein and Bliss (1973)	"
Duffy, et al. (1975)	"
Mackay and Mohtadi (1975)	Inches

* Brown, Jerry and George C. West. 1970. (eds.) Oil ecology. In: Tundra Biome Research in Alaska: The Structure and Function of Cold-Dominated Ecosystems. US IBP Tundra Biome Report 70-1. p. 75.

** Gossen, Randall G. 1973. Microbial degradation of crude oil in arctic soils. Ph.D. Thesis. Dept. Bio. Univ. Calgary, Alberta. 169 p.

TABLE 3. Guidelines used at the Alaska Agricultural Experiment Station for relating volume of oil applied per unit areas to fluid depth. These data were useful in translating oil spill experiment parameters to real spill situations and are rounded to last digit shown.

Fluid Depth	Volume Per Unit Area							
	qt/ft^2	gal/ft^2	gal/acre	bbl/acre	drum/acre	cm^3/m^2	l/m^2	l/ha
1/4 inch	.62	.155	6,789	162	123	6,350	6.35	63,500
1 cm	.98	.245	10,691	255	194	10,000	10.00	100,000
1/2 inch	1.25	.312	13,578	323	247	12,700	12.70	127,000
1.75 cm	1.71	.428	18,710	446	340	17,500	17.50	175,000
2 cm	1.96	.490	21,383	509	389	20,000	20.00	200,000
1 inch	2.49	.623	27,155	647	494	25,400	25.40	254,000
4 cm	3.92	.980	42,767	1,018	778	40,000	40.00	400,000
2 inch	4.15	1.247	45,198	1,293	987	50,000	50.80	508,000
6 cm	5.88	1.470	64,150	1,528	1,167	60,000	60.00	600,000
4 inch	9.97	2.494	108,620	2,586	1,975	101,600	101.60	1,016,000
6 inch	14.96	3.470	162,930	3,879	2,962	152,400	152.40	1,524,000
12 inch	29.92	7.481	325,860	7,759	5,925	304,800	304.80	3,048,000

TABLE 4. Selected listing of literature citations and the corresponding units of measure used to describe oil contents for terrestrial (soil) and aquatic (sediments) oil pollution studies.

Literature Citation	Units of Measure
(Volume/unit volume)	
CONCAWE Secretariat (1974)	Liters/meters^3
(Volume/unit area)	
Grummer (1965)	Liters/meter^2
(Volume/unit weight)	
Kloke and Sahm (1961)	Milliliters/kilogram
Kloke and Leh (1963)	" "
(Weight/unit volume)	
Vandenmeulen (1975)	Micrograms/liter
(Weight/unit weight)	
Johansson (1962)	(ppt) Micrograms/gram
CONCAWE Stichting (1972)	(ppm) Milligrams/kilogram
Deneke, et al. (1975)	" "
White and de Jong (1975)	(%) Grams/100 grams
Rowell (1975)	" " "
Nyborg and McGill (1975)	" " "
Udo and Fayemi (1975)	" " "
Lehtomaki and Niemela (1975)	" " "
Blauel and Lesko (1975)	Grams/gram
McGill (1975)	Gram/g oven-dry, oil-free soil
Duffy, et al. (1975)	" " " " " " "
(Weight/unit area)	
Kincannon (1972)	Pounds/foot^2

TABLE 5. Relationship of two methods used for determining an array of oil percentages in 100 grams of oil-dry soil.

Grams Oil in Sample	Sum of Soil & Oil Weight	% Oil Calculated on Oven-Dry, Soil Science Formula	% Oil Calculated, Non-Soil Science Formula	Net Difference Between Two Methods
0.001	100.001	.001	.0009	.0001
0.01	100.010	.010	.0099	.0001
0.1	100.100	.10	.0999	.0001
1.0	101.000	1.000	.9900	.0100
10.0	110.000	10.00	9.0909	.9090
25.0	125.000	25.00	20.0000	5.0000
50.0	150.000	50.00	33.3333	16.6667
100.0	200.000	100.00	50.0000	50.0000
150.0	250.000	150.00	60.0000	90.0000

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NORTH AMERICAN ARCTIC AND SUBARCTIC OIL SPILL RESEARCH IN FRESHWATER--A REVIEW

by Jacqueline D. LaPerriere

General Research Needs

The most critical need for further research on the effects of oil spills into freshwater ecosystems in the north is for the types of studies known as "baseline." In Alaska there are over 3,000,000 lakes larger than 8 hectares (20 acres) (State of Alaska, 1970). Extremely few of these lakes have been studied limnologically (Hobbie, 1973). In fact, when this author searched the published literature in 1977 for alkalinity values only about 150 were found. Most of these values resulted from a single reconnaissance visit to the particular lake.

An unpublished working document of the Alaska Pipeline Office, U.S. Department of the Interior, entitled "List of Streams and Other Water Bodies Along the Trans-Alaska Oil Pipeline Route" says, "Less than a score of the 900+ streams listed can be considered to be "known" and of these probably less than five are well known." This quote comes from a draft of the fourth revision of this document as of spring of 1977, which was close to the time when the pipeline was completed and oil began to flow. Earlier the environmental impact study of this project noted that at the time of its preparation no data existed for nearly every water body along the route.

For that pipeline it is too late to initiate "baseline" studies, but for future oil development it is not. A program akin to the Outer Continental Shelf Environmental Assessment Program (OCEAP) being administered in Alaska by NOAA for BLM to study the marine systems that may be impacted by oil development is needed for freshwater ecosystems. This program (OCEAP) is politically unique in that some effort is being made to study systems well before they undergo oil and gas lease sales and impacts must be assessed.

It will not, however, be sufficient just to conduct good "baseline" studies in the course of environmental impact studies, but commitments must be made to continue the work long enough

to allow assessments of actual, not just predicted, impacts (Rosenberg and Snow, 1977). This phase of environmental study thus far has been inadequately conducted for the Trans-Alaska Pipeline Project. Monitoring during construction was rushed and inadequate because of the dominance of the construction schedule (Fairbanks Daily New-Miner, August 18, 1979). Assessment of the effects of spills by teams of environmental scientists has been planned but not implemented.

The best approach to conduct of baseline studies would be an effort to assess regional limnology, the similarity and differences between inland waters of the same formation activity or geologic region. The concentration should be on areas likely to be impacted by planned or completed development, such as the Trans-Alaska Pipeline route and Naval Petroleum Reserve #4. The major studies which have been conducted in this manner in Alaska are of the deeper Arctic lakes which can be reached by small airplane from Barrow (Kalff, 1968; Holmquist, 1975), the major unglaciated lakes of the Tanana Valley (LaPerriere, 1978), the Tangle Lake System (Barsdate and Alexander, 1971), and the waters of the Arctic Wildlife Range (McCart, ed., 1977). Studies are currently being conducted in the Brooks Range along the Trans-Alaska Pipeline route under the R.A.T.E. project funded by NSF, but the start of these occurred after major development had taken place.

Many have believed that northern lakes are basically of one type, that is, oligotrophic with simple biological systems. Holmquist (1978) has stated after six summers exploring lakes out of Barrow:

> "The conclusion that may be drawn from my investigation is that there certainly are some young, oligotrophic, biologically simple lakes in northern polar regions, but these conditions are hardly universal or even average."

LaPerriere et al. (1975) have questioned the applicability of trophic system of lake classification in subarctic and arctic regions because of contradictory indications of state given by different parameters measured in a deep, subarctic lake.

Study of streams in Alaska is as scanty as that of lakes. There are only 27 stations included in the USGS National Water Data Network, compared to 498 in the contiguous forty-eight states, despite the fact that about one-third of U.S. river flow occurs in Alaska.

Algae

Studies on the effects of added oils on freshwater phytoplankton have been conducted in the arctic and subarctic. The results of these experiments have varied somewhat, but the common theme is of short term toxicity followed by recovery. Miller, Alexander and Barsdate (1978) in their lake experiment found longer term suppression, into the following spring, but speculate that this may have occurred because of ice action exposing the phytoplankton to fresh oil at that time.

Early work by Canadian scientists (Kauss et al., 1973) showed that oil became less toxic the longer it was weathered (exposed to air), and the volatile components became suspect. Concurrent field work conducted in Ontario showed species specific effects of oil on phytoplankton. Laboratory studies were then conducted with the alga *Chlamydomonas angulosa* and crude oil (Soto, Hellebush and Hutchinson, 1975), and with *Ankistrodesmus* spp. (8 species) and particular components of crude oil (Kauss and Hutchinson, 1975). The components tested were some of the aromatic volatiles, and these were found to be successively more toxic with decreasing solubility. However, when the eight species of *Ankistrodesmus* were treated with extracts of Norman Wells crude oil effects were seen from inhibition to stimulation. Since the algal culturers were not bacteria-free in these experiments, it is not clear whether stimulation was a result of utilization by the alga itself or by associated bacteria .

Extrapolation of laboratory results to the field is always risky because of unpredictable effects of factors which can be controlled in the laboratory. As the scientists above have noted themselves, the laboratory tests were all acute toxicity tests providing no information on the effects of chronic exposure. Additionally, in field studies where the entire community of algae is considered, the sum of the species specific effects, including perhaps the effects on the bacteria,

may give the appearance of no effect. Community photosynthesis may continue to be statistically the same as in control communities even though individual species may have disappeared and new ones appeared . Hanna et al. (1975) in subpond experiments did not find statistically significant differences between oiled and control ponds as regards the photosynthesis of phytoplankton or benthic moss though the tendency for lower values in oiled ponds was noted.

If production is temporarily decreased, there may be a dramatic increase in algal biomass when it returns to normal. This is seen to be the result of reduced zooplankton grazing, because of high zooplankton mortality due to the extreme toxicity of oil to the zooplankton. Miller et al. (1978) included in their subpond experiments some in which zooplankton were experimentally absent. They found good evidence of the importance of zooplankton grazing on reducing the algal community biomass.

In most of the studies of the effects of hydrocarbons on aquatic systems the benthic algae have been ignored. This is probably due to the great difficulty encountered in measurements on this community and the lack of standardized methods. Rosenberg and Snow (1975) noted that algae extensively colonized oiled artificial substrates which they immersed in a small river in the northern Yukon Territories to study zoobenthos effects. They did not see this growth in a comparable stream in the MacKenzie Valley, Northwest Territories. They attributed the differences in response to differences in the watershed characteristics of the two streams.

These scientists also studied the specific effects of oil on periphyton by measuring colonization onto oiled styrofoam balls and plexiglass sheets (Roeder et al., 1975). Stimulation of blue-green algae in streams was again seen. Stimulation of benthic blue-greens colonizing styrofoam substrates was also seen in experimental spills on sea-curtain divided lakes (Snow and Scott, 1975), but this was not quantified for either streams or lakes. Quantification was only attempted on diatom colonization which was not different between oiled and control areas.

Macrophytes

Only one study has specifically attempted to measure the effect of added oil on the macrophytes (vascular aquatic plants) in the north (Hanna et al., 1975). The investigators were unable to show a significant effect on the growth or chlorophyll content of a benthic moss, *Scorpidium scorpoides* (nor on the planktonic algal community). Emergent sedges, *Carex aquatilis*, and horsetails, *Equisetum fluviatile*, showed significant reduction in chlorophyll content. Limited sampling of biomass indicated a severe effect of oiling on these emergent plants.

The authors point out the likelihood that in a spill on a lake winds will move the oils to the leeward littoral zone where the emergent vegetation will be oiled, and according to their measurements, severely affected. Since this phenomenon of littoral oiling in aquatic spills has been noted by many investigators (Snow, N. B., 1975, personal communication) it is remarkable that there has been so little research on the effects of oils on aquatic macrophytes.

It is apporpriate, at this time, to emphasize the need for inventory expeditions to delineate the distribution of aquatic plants (and animals). Vast regions of the State of Alaska are unexplored concerning this aspect. Holmquist (1971) in her six summers' reconnaissance work concerning aquatic invertebrates in northern Alaska and northwestern Canada was able to extend the northward distribution range of three aquatic plants, *Lemna trisulca* (star duckweed), *Ceratophyllum demersum* (coontail), and *Myriophyllum spicatum* (water milfoil). She has noted (1974, personal communication) the inadequacy of the *Flora of Alaska and Neighboring Territories* by Hulten (1968) for the distribution of aquatic plants with many genera unreported that are definitely found in Alaska.

Zooplankton

There has been only one published paper which specifically considers the effects of oil on arctic freshwater zooplankton (O'Brien, 1978). Field studies which were focused upon the effects on algae have as mentioned above noted zooplankton effects, usually observations of complete

loss of all zooplankters noticed because of an accompanying rise in phytoplankton biomass which is due to the lack of grazing (Miller et al., 1978; Barsdate et al., 1973).

O'Brien conducted bioassay experiments and participated in an experimental spill on a pond near Barrow, Alaska. He found that relatively low doses of oil (24 ml/m^2, or approximately 10 mg/l as the water soluble fraction) were toxic to zooplankters. He found among the three organisms tested an apparent increase in sensitivity from *Heterocope septentrionalis*, a calanoid copepod, to *Daphnia middendorffiana*, a water flea, to *Branchionecta paladosa*, a fairy shrimp. This pattern was reinforced by observations of the cronology of the disappearance of these zooplankters and of *Cyclops* spp., which disappeared last, from the pond upon which the spill was conducted.

Since no concurrent analyses of the oil component concentrations were made, the specific toxicants are not known, but are suspected to be in the water soluble fraction. Subsequent bioassay experiments at Toolik Lake (Miller and Hobbie, 1976) with *D. middendorffiana, H. septentrionalis,* and *Holopedium gibberum* (another water flea) and Prudhoe Bay crude oil showed no toxicity. The researchers suspect that vigorous aeration used at Toolik Lake reduced toxicity by driving off the aqueous hydrocarbons quickly. Aeration was not used in the bioassays conducted at Barrow.

Benthic Invertebrates

Investigations of the effects of oil on northern North American freshwater invertebrates began nearly simultaneously in Alaska and Canada in 1970 and 1971, respectively. Alaskan studies have concentrated until recently on shallow thaw ponds near Barrow (Mozley and Butler, 1978) outside of any actual development area. The exception is the investigation by Nauman and Kernodle (1975) on the accidental spill at Happy Valley Creek, a tributary of the Sagavanirktok River. The Canadians, on the contrary, have concentrated mainly on stream studies. These were conducted within the MacKenzie and Porcupine River watersheds, areas of potential development. Some lakes of the MacKenzie Delta were also considered.

The Alaskan stream study is merely speculative in that neither the oil concentration nor the benthic invertebrates were actually quantified. Surber sampling which was used requires intense replication due to the patchy distribution of benthic invertebrates. Recent studies (Coleman and Hynes, 1970; Hynes, 1974) have discovered that significant quantities of stream animal benthos may be found deep within the streambed of stony streams, deeper than is disturbed in Surber sampling. Still, in the study of pollution of a stream, upstream and downstream comparisons of Surber samples are often used; more intense sampling than three samples per station are, however, recommended. It is also recommended to sample at a station set in the zone where complete recovery is expected, that is, where evidences of pollution are no longer observed. This is done routinely to assure that what one is measuring are pollutional effects, not just downstream effects. This station should have a fauna comparable to the station(s) set upstream above the pollution source. It may be necessary to use several of these downstream stations if one does not have immediate measurements of the concentration of the pollutant to assure the placement of at least one in the zone of recovery. This study had no such station.

One statement in the Discussion section of this paper needs comment. The authors state: "Benthic invertebrates usually are immobile and are unable to escape deleterious environmental changes." The phenomenon of invertebrate drift in which the invertebrates move downstream has been known and studied for about twenty years. For reviews of this research see Waters, 1972 and Muller, 1974). One response that stream macroinvertebrates have to pollution is to increase their drift rate, in what Waters (1972) calls "catastrophic drift." Another statement of these authors which should be addressed is that, "Cladocera generally are not considered indicators of environmental stress." Reference to the Zooplankton Section of this review paper will show that cladocerans are quite sensitive to oil pollution with the water soluble fraction probably containing one to several toxicants.

Canadian studies consisted both of experimental spills, and experimental placement of oiled artificial substrates to measure colonization effects. Due to the dominance of the benthic com-

munity by chironomids (Dipitera: non-biting midges) much attention was focused on this family. Indicator species were found that had both negative (e.g. *Nilotanypus fimbriatus* [Walk.]) and positive (e.g. *Cricotopus bicintus* [Meig.]) responses to oil (Rosenberg and Wiens, 1976). The search for indicator species among the chironomids included identification of over 150,000 specimens, and a key to primarily the genus level illustrated with microphotographs was produced (Oliver, McChymont, and Roussel, 1978) for the investigated streams and lakes of the Mackenzie and Porcupine watersheds as well as for a few lakes outside the area near Tuktoyaktuk, N.W.T.

In one of the slower streams the artificial substrates became overgrown with blue-green algae which undoubtedly masked the oil effects. These overgrown substrates seemed to attract chironomids. Rosenberg and Snow (1975) speculate that older weathered oil may be food for some chironomids, and so, an attractant. Or the attraction may be a function of some effect of the algal growth. In faster streams colonization of the oiled substrates by zoobenthos was retarded.

The lake and pond studies have been so few that major conclusions cannot be reached. As Mozley and Butler (1978) point out for their studies pond to pond variation of benthic populations, and their variations over time are so high that oil effects cannot be separated conclusively. The U.S. and Canadian groups (Snow and Scott, 1975) both report some common conclusions from their observations. Both note species specific effects for various chironomids, and both noted entrapment of organisms in the leeward littoral as the spill oil was moved by the winds. The major difference between the two groups was that the Canadians noted high larval mortality among negatively affected chironomids, while the U.S. scientists did not measure a like mortality, but found reduced emergence. They speculate that the oil may have some effect on metamorphis.

Laboratory experiments on toxicity of oil to benthic invertebrates conducted at Barrow found no toxic effects. No analysis of oil concentrations in the test solutions are reported. Aeration of the test aquaria may have driven off the volatile hydrocarbons.

Fishes

To date only Morrow (1974), and Moles and his associates (1979) have tested Alaskan freshwater and anadromous fishes for their sensitivity to crude oil and some of its components. Both have conducted static acute toxicity tests. Moles et al. (1979) discuss the differences to be expected in flow-through acute toxicity tests. Chronic toxicity tests have not been reported for these fishes, but some are being conducted (J. Schwartz, 1979, personal communication).

Morrow's study on coho and sockeye salmon (*Oncorhynchus kisutch* and *O. nerka*) was conducted without actual measurement of oil concentrations in the test solutions. It is understood that these measurements are difficult and expensive, but standard acute toxicity testing methods (A.P.H.A. et al., 1976) require testing of toxicant concentration in the test solutions at the beginning and at least once during the test. Morrow's study was conducted in a 30% salt solution and not freshwater. It is possible that diseased fish were used as test organisms in this study. Morrow reports clubbing of gill filaments in both control and test organisms, and dismisses several possible explanations. About one year after his experiments I received some coho salmon from the same source for testing of thermal effects, and found them to have evidence of chronic bacterial gill disease.

Moles et al. (1979) determined the 96-hour median tolerance limit (TL_m) of various life cycle stages of young salmonids, and of adult threespine sticklebacks (*Gasterosteus aculeatus*) and juvenile slimy sculpins (*Cottus cognatus*) to Prudhoe Bay crude oil and to benzene. Early life cycle stages from eggs to fry of pink (*Oncorhynchus gorbuscha*) and coho (*O. kisutch*) salmon were tested for sensitivity to benzene. Eggs were quite insensitive and sensitivity increased with life cycle stage. The investigators point out that in uptake of hydrocarbons by very young fishes the yolk takes up most of the hydrocarbons. As these are slowly used up metabolically the young fish is exposed to the dose gradually. Once the yolk reserve is gone the fish becomes much more sensitive to hydrocarbons.

The salmonids tested (Dolly Varden char, *Salvelinus malma*; arctic char, *S. alpinus*; arctic grayling, *Thymallus arcticus*; sockeye salmon, *O. nerka*; pink salmon, *O. gorbuscha*; coho salmon, *O. kisutch*; and chinook salmon, *O. tshawytscha*) and the slimy sculpin were found similarly sensitive to both crude oil and benzene. The threespine sticklebacks were found to be far less sensitive. The crude oil 96-hour TL_m's ranged from 2.75 mg/l total aromatic hydrocarbons for Dolly Varden char to 10.45 mg/l for threespine sticklebacks. Benzene 96-hour TL_m's ranged from 11.96 g/l for Dolly Vardens to 24.83 g/l for threespine sticklebacks.

Out-migrants of pink, and sockeye salmon and Dolly Varden were acclimated to seawater and tested for sensitivity to oil. These were found about twice as sensitive as those fishes when tested in freshwater. The authors, eliminating differences in toxicant concentration or character by chemical analysis of the toxicant in the two types of water, believe that the stress of rapid acclimatization to seawater makes the fishes more susceptible to oil effects. They speculate that salmonids fully adapted to seawater may be again less sensitive. This finding has management implications in that an oil spill in an estuary during migration of salmonids may have a greater toxicity effect than at other locations and at other times in these fishes life cycles.

Synthetic tri-aryl phosphate synthetic oils, which are fire resistant, are expected to be used as lubricants at pump stations along proposed gas pipelines. Toxicity testing has been conducted with a commercial brand of this oil on fishes (Lockhart et al., 1975; Wagemann, 1975). In a static acute toxicity test common guppies (*Poecilia reticulata*) were not affected in 24 hours in a saturated solution. However, chronic toxicity tests on rainbow trout (*Salmo gairdneri*), exposed to 0.9 mg/l on the average, showed effects. After 8 days the fish were less active and by 14 days they had stopped surface feeding. At about 4 months of exposure the fish began to die. Necropsy showed enlarged livers, and discoloration of internal tissues. Increases in activities of lactate dehydrogenese and glutamic oxalacetic transaminase were measured in exposed fish.

Decomposers

As with the other communities considered, little research specific to oil contamination of northern freshwater ecosystems has been conducted on the microbes important in decomposition. Bergstein and Vestal (1978) conducted studies near Barrow, Alaska, in small enclosures placed in tundra ponds, and also examined tundra ponds which had been oiled 2 and 7 years previously. Jordan et al. (1978) studied a lake, 240 km south of Prudhoe Bay, along the Trans-Alaska pipeline, wherein a sea-curtain isolated a small section of the lake which was oiled.

Bergstein and Vestal (1978) concluded that spilled oil did not significantly alter the water or sediment microflora during short or long terms. Neither toxic nor stimulatory effects were seen that were accepted. Apparent stimulation was noted for some oiled plexiglass cores set up 2 years previously, but the authors suspect container effects.

Jordan et al. (1978) similarly found no short term toxic effects of oil on either the microflora of the water column or of the sediments. It should be noted, however, that no measurements are reported until several months after the spill. They did, however, find significant stimulation during June of the following summer. This difference in findings between the two studies may be due to the fact that Bergstein and Vestal (1978) only used plating techniques for enumeration, while Jordan et al. (1978) used the more accurate acricline orange direct count technique of Hobbie et al. (1977). Direct counting techniques, of which the acricline orange is the most sophisticated since it differentiates live and dead cells, have been shown to obtain counts which may be several orders of magnitude greater than those of plating techniques (Jannasch and Jones, 1959). Plating techniques are acceptable if a direct relationship between them and direct counts is shown.

Both groups report on degradation of labeled hydrocarbons (naphthalene and hexadecane). Bergstein and Vestal (1978) tested the microflora of the water of their subponds for this ability, and Jordan et al. (1978) tested the microflora of sediments diluted into filtered lake water. Bergstein and Vestal assume they were measuring mineralization of the labeled hydrocarbons,

while Jordan et al. more cautiously only report the results of experiments to measure net uptake of the labeled compounds by the microflora. They discounted all the results of their attempts at mineralization experiments because of methodology problems. Bergstein and Vestal (1978) were using a similar method, and may have avoided the problems discussed by Jordan et al. (1978). By adding the scintillation fluid and counting the disintegrations by the next day, they avoided the problem of losing the labeled CO_2 which the other team faced because of the remote field location which required stockpiling and shipment of samples to a distant laboratory for counting. However, they may have not avoided the other problem of hydrocarbon contamination of the CO_2 absorbant because they report no vigorous attempts to drive off the hydrocarbons, e.g. by bubbling with air while the labeled CO_2 was trapped as CO_3 in a basic solution. They note only an additional two hour incubation of the samples after the strong base had been added. If the vials were capped as in the previous incubations it is likely that labeled hydrocarbons remained in the vials with the potential to contaminate the CO_2 absorbant in the next step, during which labeled CO_2 was released by acidification and subsequently adsorbed.

Jordan et al. (1978) found little difference in degradation ability for populations previously exposed to oil as compared to controls. Both groups report that naphthalene was degraded more slowly than hexadecane. There is a possibility that with lower concentrations of added substrates they may have found the opposite. Dr. D. K. Button and Ms. B. Robertson, testing oil-exposed estuarine flora found the rate of degradation of naphthalene faster than that of benzene and toluene (B. Robertson, 1979, personal communication). Incidentally, the substrate concentrations reported in Table 5 of Jordan et al. (1978) are probably incorrect, all being high by a factor of 100. The concentrations reported in the text of the methods section are 100 times lower and can be calculated from the specific activities given and the dilutions they performed.

It can be recommended from the apparent conflicting results of the two studies and from the recommendations of Jordan et al. (1978) that further hydrocarbon degradation studies be conducted. Further studies, however, should use more concentrations of the substrates, attempt-

ing to cover well the entire range between zero level additions and those which have toxic effects. Incubation times also should be varied. Measurable oxidation often begins within a short time of addition of the substrate, minutes or hours, not days (E. J. Brown, 1979, personal communication).

Both groups attempted to evaluate the effects of oil (oil and fertilizers in the case of Bergstein and Vestal) on heterotrophic uptake of glucose. Jordan et al. did not find a difference between oiled and unoiled water or sediment floras in this activity. Bergstein and Vestal did not measure any significant differences between any of their subpond treatments including controls, oiled, and oiled and fertilized.

Bergstein and Vestal in their enumeration studies found that the addition of oleophilic phosphate fertilizer stimulated bacterial populations in subponds that were both oiled and unoiled as measured by plating techniques. They did not see the same effect when the same concentration of phosphorus was added as inorganic P. This finding agrees with that of an earlier study by Atlas and Busdosh (1976) who found that oleophilic phosphorus and nitrogen fertilizers stimulated in situ degradation of Prudhoe crude oil. They suggest that perhaps in accidental spills on tundra ponds, therefore, this fertilizer might be added to speed recovery. While they advise further studies of the effect of this fertilizer on other communities before it is used in this way, it is important to note that they found the fertilizer to be ". . .an excellent detergent (which) dispersed the oil scum."

The use of detergents, which may not themselves be toxic, to disperse oil which is toxic throughout the water column has been cautioned against (Mozley and Butler, 1978) because of the possibility that it will expose communities (such as the benthos) which might otherwise be isolated from the oil and its effects. Bergstein and Vestal conclude that the hydrocarbon end of the fertilizer molecule (2-ethylhexyldipolyethylene oxide phosphate) rather than the phosphate is stimulatory. This could be tested by conducting experiments in which the phosphates on the polymer were substituted for by ions that are less biologically active, or rarely found to be in limiting concentration, such as sulfates.

Horowitz and Atlas (1977) and Horowitz et al. (1978) have studied the effect of the leakage of a refined product, leaded MOGAS (gasoline) into the water supply pond at the Naval Arctic Research Laboratory located at Barrow, Alaska. The leak has occurred in a gravel-buried pipeline and seeped to the pond. These authors found that the gasoline continued to spread even to sites they had chosen as controls in the first year's study. They speak of finding hydrocarbons persisting in the gravels a year later, however, this may be a function of fluid transport (which they have not evaluated), as well as the slow degradation of the gasoline which they have measured.

They have used plating techniques for testing for the relative presence of hydrocarbon utilizers to indicate hydrocarbon contamination. They have also used them to infer numbers of hydrocarbon degraders present in situ. Again, the relationship between plate counts and population numbers should be demonstrated by comparison to a direct counting method.

Their study of addition of fertilizer to the gravels at specific sites, in which they conclude that the addition of fertilizer stimulated hydrocarbon degradation, lacks replication. They discuss that the unfertilized site was higher over the season in concentration of hydrocarbons and that both sites lost hydrocarbons as the season progressed. It is perhaps premature, then, for their recommendation of fertilization to speed degradation since this may promote the growth of nuisance blooms of algae that will further degrade the water quality of this water supply. The work they report on the effects of gasoline on nitrogen cycling is inconclusive.

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SURVEY OF HYDROCARBON SPILLS REPORTED IN ALASKA 1974 THROUGH MAY 1976

Jay D. McKendrick

INTRODUCTION

Research is usually considered as an investment because findings eventually bring returns and benefits. While in the process of reviewing the research literature of terrestrial oil spill reclamation technology for Alaska, it was noted that most studies had been devoted to crude oil. The popular news contained a preponderance of reports on refined petroleum product spills in Alaska, and few, if any, notices of crude oil spills. That inconsistency indicated a need to reevaluate oil spill reclamation research priorities for Alaska. Consequently, a survey of reported spills was undertaken to identify the nature and types of hydrocarbons spilled on terrestrial sites in Alaska.

METHODS

The cooperation of the U.S. Environmental Protection Agency office in Anchorage, Alaska, was enlisted in 1976. The various reports of spills filed with that office were compiled on punch cards for the period 1974, when spill reporting commenced, through May 1976. Type and amount of material spilled, date, location, and size of the area affected were recorded from those various reports. The cards were sorted according to the above criteria and spot checked to estimate duplication errors. Duplicate reports were usually found in the files because the spills were sometimes reported first by telephone and later in writing. Sometimes the written report was delayed for a time and hence, appeared much later in the chronology of the files than the notation of the telephoned report. One other known error was the omission of the volume and size of area for a major heating oil leak at one of the pipeline construction camps. This probably occurred because the total extent and nature of the spill could not be determined immediately.

During this survey, those reports to EPA constituted the entire collection to date for Alaska. During the study period, the trans-Alaska pipeline construction started, which represented the largest single construction effort in the state's history and as a consequence require large quantities of fuel and other hydrocarbons. Most of the oil spills reports were related to that project. Obviously, other activities in Alaska were creating spills, but the practice of reporting

spills was just starting. Because the trans-Alaska pipeline project was under close scrutiny by the media and regulatory agencies, there was a significant effort to comply with regulation policies by most pipeline-related groups.

Public reaction to the regulations requiring "voluntarily" reporting of hydrocarbon spills for which the "volunteer" could later be fined and legally prosecuted may have biased the reports. It is reasonable to assume a natural tendency to avoid self-incrimination.

Over-reaction, the opposite extreme, was also apparent. Many of the reports were for minor oil leaks. Volumes as low as 1/10 pint and covering two inches^2 were reported, possibly because either regulations were unclear or in hopes that such trivia would create unnecessary paperwork, thus registering a complaint to the regulatory agency. In this survey, only spills of 50 gallons or more or those affecting 1,000 square feet or more were arbitrarily considered significant in terms of environmental degradation. All spill reports, regardless of size, were counted in the total number.

RESULTS

Table 6 shows there was 7,890 spills affecting 32.97 acres (13.35 ha), during the 29-month period surveyed. Total gallons spilled was 460,104 (121,592 l.), for an average rate of 13,955 gallons/acre (0.91 l/m^2).

Spill reporting increased over time (Table 7). Part of that increase was probably due to increasing awareness of the public for the need to report spills. There was also a concurrent increase in the trans-Alaska pipeline construction and the use and handling of petroleum products in Alaska during the 1975 and 1976 period compared to prior years, escalating the probability of spills.

Diesel and fuel (heating) oils were the majority of products spilled (Table 7). If only the significant spills were considered from this survey, diesel and lubrication oil spills outranked the other substances in relative numbers (Table 8). Unfortunately, diesel spills cause substantial damage to soils and plant life (Everett, 1978). Long-lasting effects from contamination of diesel and heating fuels are commonly evident in Alaska. Many fuel storage depots and homesites where oil-fired heating is used have one or more patches of "killed" soil from leakages.

According to the literature, research on refined hydrocarbon spills in Alaska has focused mainly on describing their impacts and persistences (Deneke, et al., 1975; Everett, 1978; Sexstone, et al., 1978). Spilled diesel is known to persist for at least three decades, and if

great enough, it can prevent reinvasion by higher plants (Everett, 1978). Crude oil and certain other hydrocarbon spills examined in that same study were less damaging over time than diesel.

In conclusion, findings from this survey and the literature suggest a potential benefit from technology to mitigate diesel and heating oil spill damages in Alaska. The area of many such spills is undoubtedly small and may be mistakenly judged as inconsequential compared to more spectacular crude oil spills. However, in terms of annoyances to human environments and threats to domestic water and food supplies, these refined hydrocarbons are apt to be a greater problem than crude oil spills which often occur in uninhabited regions. Consequently, small-scale, but long-term investigations for mitigating diesel and heating oil spills should receive appropriate consideration in Alaska.

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TABLE 6. Number*, volume, and area affected from terrestrial oil and hydrocarbon spills reported to the Anchorage Environmental Protection Agency office during 1974 through May 1976.

Spill Material	Number of Reported Spills	Gallons Spilled	Area Affected (acres)
Diesel	1,502	349,811	25.3
Fuel oil	109	67,135	0.2**
Aircraft fuel	59	1,850	0.1
Hydraulic fluid	2,308	15,202	2.1
Lubrication oil	3,073	15,973	2.9
Gasoline	96	6,643	0.1
Antifreeze	170	820	0.07
Misc. & unknown	573	4,310	2.2
Totals	7,890	460,104	32.97

* Reports included approximately 5% duplication.

** Area affected was not reported for at least one major spill; therefore, this estimate is unrealistic.

TABLE 7. Gallons by year of various oils and hydrocarbon products reported spilled to the Anchorage Environmental Protection Agency office for the period 1974 through May 1976.

Spill Material	Number of Gallons Reported Spilled by Year			Total for Period	Percentage of Volume Spilled
	1974	1975	Through May 1976		
Diesel	28,285	216,045	86,249	330,579	82.1
Fuel oil	0	65,950	0	65,950	16.4
Aircraft fuel	55	150	205	410	0.1
Hydraulic fluid	0	225	226	451	0.1
Lubrication oil	110	820	1,264	2,194	0.5
Gasoline	0	0	2,700	2,700	0.7
Miscellaneous	0	90	0	90	0.1

TABLE 8. Numbers* by year of significant oil and hydrocarbon product spills (those either greater than 50 gallons or affecting more than 1,000 sq. ft.) reported to the Anchorage Environmental Protection Agency office the 1974 through May 1976 period.

Spill Material	Numbers of Reported Spills		
	1974	1975	Through May 1976
Diesel	35	91	71
Fuel oil	0	5	0
Aircraft fuel	2	1	2
Hydraulic fluid	0	5	8
Lubrication oil	1	9	23
Gasoline	0	0	1
Miscellaneous	0	1	0
Totals	38	112	105

* Numbers corrected to eliminate duplicated reports.